XAFS analysis on the interaction between RuO₂/CeO₂ and C₃H₆

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INTRODUCTION

CeO₂ is an evitable component in the automobile catalyst; it keeps high surface area, prevents sintering of noble metals, and thus, stabilizes their dispersed state. We found that the amount of C₃H₆ adsorbed on RuO₂/CeO₂ was peculiarly larger than those on Pt-, Pd-, and Rh/CeO₂. The interaction between RuO₂/CeO₂ and C₃H₆ was investigated by XAFS analysis.

EXPERIMENTAL

Ce(OH)₃ was precipitated from aqueous Ce(NO₃)₃ with NaOH at pH of about 11. The precipitate while it was wet, was dispersed in deionized water. A known amount of RuCl₃ was added followed by introducing HCHO under stirring at 90 °C for 1 h. Then 3 N-NaOH was added to the mixture until the pH of the solution was about 11. The solid portion was filtered and washed with deionized water followed by drying at 80 °C overnight and calcination at 500 °C for 3 h in air. XAFS measurements were carried out using a reaction cell. RuO₂/CeO₂ was pretreated with O₂ at 200 °C for 1 h, was cooled to room temperature and the spectra were recorded. Then, the cell was evacuated to remove O₂, C₃H₆ was introduced on the catalyst for 15 min at room temperature and the spectra were also recorded.

RESULTS AND DISCUSSION

The Ru K-edge XANES spectra are shown in Fig. 1. The pre-edge peak was not detected in RuO₂ but it was observed at 22115 eV for the RuO₂/CeO₂ pretreated with O₂. The pre-edge peak is caused by the transition from 1d to 4d level of metal ions. Although this transition is formally forbidden, asymmetric configurations of metal ions allow it. As RuO₂ has a good symmetry with six coordinated structure, the pre-edge peak is not detected. However, as the pre-edge peak was detected in the O₂-treated RuO₂/CeO₂, we deduced that the state of the Ru species was more asymmetric than RuO₂ and was in a five-coordinated structure. When C₃H₆ was introduced to the RuO₂/CeO₂, the pre-edge peak was disappeared. Therefore, the Ru species with the five coordinated structure on CeO₂ reacted with C₃H₆ and Ru seemed to change to six coordinated structure.

The FT peak intensity of RuO₂/CeO₂ pretreated with O₂ was lower than that of RuO₂ and the peak pattern of RuO₂/CeO₂ was different from RuO₂ in the region of 3.0 Å(Fig. 2). Therefore, we considered that two Ru species were dispersed on CeO₂: the most of Ru species formed RuO₂ and a part of Ru species highly dispersed on CeO₂ formed Ru-O-Ce bonds. The FT’s of RuO₂/CeO₂ after introduction of C₃H₆ is similar to RuO₂. Therefore, the oxygen atoms of Ru-O-Ce bonds were reacted with C₃H₆ but Ru-O-Ru in RuO₂ was not reacted and remained. From this results, we consider that RuO₂/CeO₂ pretreated with O₂ have highly dispersed Ru species on CeO₂, which forms Ru-O-Ce. This is in the five coordinated structure and reacts with C₃H₆.

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